

NO DRAWINGS

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(54) PROCESS FOR ALKYLATING DIHYDROXY BENZENES

(71) We, UNION RHEINISCHE BRAUN-KOHLN KRAFTSTOFF AKTIENGESellschaft, a body corporate organised under the laws of Germany, of Postfach 8, 5047 Wesseling, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for alkylating dihydroxy benzenes.

It is known that pyrocatechols can be alkylated for example, with isobutylene in the presence of catalysts. As is normally the case with alkylation reactions, acid compounds such as sulphuric acid, phosphoric acid, zinc chloride or cation exchangers are generally used as the catalysts in this process.

The present invention provides a process for producing dihydroxy mono- and di-alkyl-benzenes which comprises reacting a dihydroxy benzene with an olefin containing from 2 to 4 carbon atoms, alcohol or ether as alkylating agent at a temperature of from 50 to 150°C, in the presence of an acid-activated but acid-free bleaching earth as catalyst.

The reaction is preferably carried out over a period of from 1 to 12 hours, depending both upon the temperature selected and upon the quantity of catalyst used. As a rule, this does not have to be more than 5% by weight, based on the dihydroxy benzene used.

The accumulation of dialkyl dihydroxy benzenes can be controlled by variation of the molar ratio of dihydroxy benzene to alkylating agent. If a particularly high proportion of monoalkylated compounds is required, the molar ratio should not be any higher than 1:0.7.

It is essential to free the bleaching earth catalyst to be used from the acid adhering

to it following activation because, in this way, it is possible to increase the activity of the catalyst. Thus, when an acid-activated bleaching earth still containing small quantities of acid was used, the yield of *p*-tert. butyl pyrocatechol, for example, fell by some 10% compared with the yield which it was possible to obtain with the corresponding acid-free bleaching earth.

The reaction can optionally be carried out in a solvent, for example cyclohexane or heptane. The process according to the invention enables alkyl dihydroxy benzenes to be obtained with improved economy because the catalyst used is very easy to recover and there is no need to use the elaborate apparatus required when acids are used.

An acid-free bleaching earth was used in the following Examples, in which all percentages are by weight, unless otherwise indicated.

Example 1

220 g of pyrocatechol and 4.4 g of bleaching earth were heated to 120°C. 56 g of isobutylene (molar ratio of pyrocatechol to isobutylene 1:0.5) were introduced into this mixture with intensive stirring in such a way that the entire olefin was absorbed over a period of 1.5 hours. An alkylate of the following composition was obtained:

45.0% of pyrocatechol,	
52.7% of <i>p</i> -tert.butyl pyrocatechol,	
1.1% of 4,6- and 3,5-di-tert.-butyl pyrocatechol	80
and	
1.2% of residue.	

Example 2

The procedure was as described in Example 1, the alkylating agent being isobutanol instead of isobutylene. On this occasion the reaction temperature was 150°C, whilst the catalyst was used in a quantity of 0.2% based on the pyrocatechol used. The molar ratio of pyrocatechol to

isobutanol was 1:0.8. The alkylate had the following composition:

26.0% of pyrocatechol,

53.0% of *p*-tert.butyl pyrocatechol,

5 15.6% of 4,6- and 3,5-di-tert.butyl pyrocatechol,

and

5.4% of residue.

Example 3

10 The procedure was as described in Example 1 except that, on this occasion, the molar ratio of pyrocatechol to isobutylene was 1:1.35. Analysis of the reaction product revealed:

15 58.4% of pyrocatechol,

36.5% of 4,6- and 3,5-di-tert.butyl pyrocatechol,

and

5.1% of residue.

Example 4

Pyrocatechol was suspended in cyclohexane and the resulting suspension was alkylated at 75°C as described in Example

1. The molar ratio of pyrocatechol to isobutylene was 1:0.7. All the pyrocatechol

25 had entered into solution on completion of alkylation. Analysis revealed the following composition of the alkylate:

31.0% of pyrocatechol,

30 56.5% of *p*-tert.butyl pyrocatechol,

7.4% of 4,6- and 3,5-di-tert.butyl pyrocatechol,

and

5.1% of residue.

Comparative Example 4

When alkylation was carried out in the presence of a bleaching earth containing a little acid, only 43.8% of *p*-tert.butyl pyrocatechol were obtained.

Example 5

Pyrocatechol was alkylated with propylene under its own pressure at 200°C in an autoclave in the presence of 5% of bleaching

45 earth, based on the pyrocatechol used. The molar ratio of pyrocatechol to propylene was 1:0.85, and the reaction time was 2

hours. Analysis of the alkylate by gas chromatography produced the following result:

50 31.3% of pyrocatechol,

1.2% of pyrocatechol monoisopropyl ether,

28.0% of isopropyl pyrocatechol,

37.8% of diisopropyl pyrocatechols, and

55 1.7% of residue.

Example 6

Hydroquinone was alkylated with iso-

butylene in an autoclave at 180°C in the presence of 2% of bleaching earth, based on the hydroquinone used. The molar ratio 60 of hydroquinone to isobutylene was 1:0.65. Working up and analysis of the crude alkylate were carried out as described in Example 1. The following results were obtained: 65

36.5% of hydroquinone,

43.9% of tert.butyl hydroquinone,

13.6% of 2,5-di-tert.butyl hydroquinone, and

6.0% of residue. 70

WHAT WE CLAIM IS:—

1. A process for producing dihydroxy mono- or di-alkyl-benzenes which comprises reacting a dihydroxy benzene with an olefin 75 containing from 2 to 4 carbon atoms, alcohol or ether as alkylating agent at a temperature of from 50 to 150°C, in the presence of an acid-activated acid-free bleaching earth as catalyst. 80

2. A process as claimed in claim 1 wherein reaction is carried out over a period of from 1 to 12 hours.

3. A process as claimed in claim 1 or 2 wherein the amount of catalyst is up to 5% by weight, based on the dihydroxy benzene used. 85

4. A process as claimed in any of claims 1 to 3 wherein reaction is carried out in a solvent. 90

5. A process as claimed in claim 4 wherein the solvent is cyclohexane or heptane.

6. A process as claimed in any of Claims 1 to 5 wherein the molar ratio of dihydroxy benzene to alkylating agent is no higher than 1:0.7. 95

7. A process as claimed in Claim 1 substantially as hereinbefore described.

8. A process as claimed in Claim 1 100 substantially as described with reference to any of the Examples.

9. Dihydroxy alkyl-benzenes when produced by a process as claimed in any of the preceding claims. 105

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